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Vapor−Liquid Equilibria of Methanol, Ethanol, Propan-2-ol, and 2-Methylpropan-2-ol with a Five-Component Hydrocarbon Mixture at 101.3 kPa

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Isobaric vapor−liquid equilibria (VLE) were measured at 101.3 kPa for the systems of methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol separately with a five-component hydrocarbon mixture. The relative volatilities of alcohol with respect to the hydrocarbon mixture were also derived. Analysis of the experimental VLE data exhibits a minimum boiling temperature for all the systems. The experimental data have been correlated with the mole fraction of alcohol using the Redlich−Kister and Wisniak−Tamir equations.

Introduction

Reformulated gasoline includes certain oxygenated compounds such as alcohols and ethers. These are mostly methanol, ethanol, propanols, and butanols and methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline and there is an increasing interest in the thermodynamic behavior of these components in a hydrocarbon mixture. However, there are relatively few vapor−liquid equilibrium data on oxygenate + multicomponent hydrocarbon mixtures. Such data are important for predicting the vapor-phase composition that would be in equilibrium with different hydrocarbon liquids.

For these reasons, we measured vapor−liquid equilibrium (VLE) data for the systems of methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol separately with a five-component hydrocarbon mixture at 101.3 kPa. The hydrocarbon mixture is a simulated gasoline and contains hexane, heptane, 3-methylpentane, methylcyclohexane, and *p*-xylene. The equilibrium data are used to calculate the relative volatilities of alcohol with respect to the hydrocarbon mixture. The equilibrium vapor-phase compositions of alcohol and the boiling temperatures have been fitted with the Redlich−Kister and Wisniak−Tamir equations to estimate the coefficients. For these systems no VLE data have been previously reported.

Experimental Section

The chemicals used were of analytical grade and obtained from Fisher, Tedia, and Merck. All alcohols were dried over molecular sieves (Aldrich, 0.3 nm) and all chemicals were used without further purification. The purity of all chemicals was checked by gas chromatography. In all cases, chemicals with a purity greater than 99.6 mass % were used for the experimental investigations. The purity of solvents was further ascertained by comparing their densities, refractive indices, and boiling points, which agreed reasonably with the corresponding literature values[1] (Table 1). Densities, ρ, of pure compounds were measured at (298.15 ± 0.01) K using a DMA-58 vibrating-tube densimeter (Anton-Paar, Graz/Austria) with an uncertainty of ±0.02 $\mathrm{kg \cdot m^{-3}}$. Refractive indices, n_D, of pure chemicals were measured at (298.15 ± 0.1) K by an Abbe refractometer, Atago RX-5000 (ATAGO, Tokyo/Japan), with an uncertainty of ±0.000 01 units.

The VLE measurement apparatus was an all-glass equilibrium still (NGW, Wertheim/Germany) with provisions for both vapor and liquid recirculation as described by Hunsmann.[2] The still has a total capacity of about 100 $\mathrm{cm^3}$. The charge for experimental runs was prepared by mixing known masses of alcohol with a simulated gasoline base fuel which contains 15.0 mol % hexane, 15.1 mol % heptane, 15.1 mol % 3-methylpentane, 41.0 mol % methylcyclohexane, and 13.8 mol % *p*-xylene. The base fuel has an average molecular weight of 95.98 and a refractive index of 1.410 26 at 298.15 K. A set of 19 compositions was prepared with an increment of 0.05 mole fractions for each system. Equilibrium conditions were indicated by constant boiling temperatures of the liquid and vapor phases within the equilibrium cell and a difference less than 0.02 K. The system was allowed to maintain this equilibrium state for about 1 h before samples were taken.

The equilibrium boiling temperature was measured with a digital thermometer (Hart Scientific Model 1560/5644, UT/USA) with an accuracy of ±0.005 K. System pressure was regulated through a manostat pressure control. To facilitate the manostat pressure control and to give it more accuracy, a modified Świętosławski ebulliometer[3] was built to measure the boiling point of pure water. During an experimental run, the system was maintained at the pressure when the temperature reading on the ebulliometer became equivalent to 373.15 K with an uncertainty of ±0.02 K. System pressure could then be controlled at 101.3 kPa and measured with an uncertainty of ±0.1 kPa. The uncertainty of equilibrium boiling-temperature measurements was estimated to be ±0.06 K.

Equilibrium compositions of sampled liquid and condensed vapor phases were analyzed with a Perkin-Elmer Autosystem gas chromatograph (GC). A flame ionization detector was used along with a (60-m long, 0.25-mm i.d., 0.5-μm film) capillary column packed with Petrocol DH

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Table 1. Normal Boiling Points, *T*, Densities, *ρ*, and Refractive Indices, n_D, at 298.15 K for the Chemicals Used in This Study

compound	*T* (K) this work	*T* (K) lit.[1]	*ρ* (kg·m^{-3}) this work	*ρ* (kg·m^{-3}) lit.[1]	n_D this work	n_D lit.[1]
methanol	337.58	337.70	786.68	786.37	1.32685	1.32652
ethanol	351.43	351.44	785.30	784.93	1.35948	1.35941
propan-2-ol	355.40	355.39	781.20	781.26	1.37517	1.3752
2-methylpropan-2-ol	355.47	355.497	780.80	781.2	1.38486	1.3852
n-hexane	341.86	341.866	654.93	654.84	1.37231	1.37226
3-methylpentane	336.41	336.432	659.60	659.76	1.37399	1.37386
n-heptane	371.55	371.574	679.47	679.46	1.38537	1.38511
methylcyclohexane	374.05	374.084	764.91	765.06	1.42076	1.42058
p-xylene	411.53	411.509	856.54	856.61	1.49306	1.49325

Table 2. Experimental VLE Data at 101.3 kPa for the System Methanol (1) + 3-Methylpentane (2) + *n*-Hexane (3) + *n*-Heptane (4) + Methylcyclohexane (5) + *p*-Xylene (6)

i	x_i	y_i	γ_i	x_i	y_i	γ_i	x_i	y_i	γ_i
		352.96 K			330.58 K			330.59 K	
1	0.018	0.268	8.385	0.359	0.694	2.569	0.758	0.699	1.225
2	0.146	0.228	0.955	0.115	0.102	1.069	0.036	0.101	3.381
3	0.111	0.165	1.075	0.106	0.077	1.052	0.039	0.078	2.896
4	0.142	0.088	1.110	0.103	0.054	2.093	0.036	0.052	5.764
5	0.430	0.221	0.967	0.181	0.058	1.317	0.082	0.057	2.856
6	0.153	0.030	1.282	0.136	0.015	1.830	0.049	0.013	4.401
		346.42 K			330.56 K			330.69 K	
1	0.042	0.420	7.143	0.366	0.694	2.522	0.808	0.701	1.148
2	0.144	0.189	0.968	0.113	0.102	1.089	0.026	0.100	4.620
3	0.127	0.143	0.987	0.104	0.077	1.073	0.029	0.077	3.832
4	0.139	0.068	1.093	0.099	0.054	2.179	0.032	0.052	6.459
5	0.378	0.161	0.994	0.201	0.059	1.207	0.065	0.057	3.590
6	0.170	0.019	0.945	0.117	0.014	1.987	0.040	0.013	5.367
		340.30 K			330.54 K			331.03 K	
1	0.074	0.536	6.525	0.503	0.697	1.844	0.863	0.703	1.062
2	0.141	0.148	0.930	0.081	0.103	1.535	0.019	0.100	6.252
3	0.125	0.113	0.956	0.072	0.078	1.571	0.022	0.077	4.994
4	0.130	0.065	1.387	0.064	0.053	3.311	0.028	0.052	7.286
5	0.347	0.119	0.989	0.180	0.057	1.304	0.043	0.056	5.263
6	0.183	0.019	1.129	0.100	0.012	1.995	0.025	0.012	7.806
		333.63 K			330.50 K			331.87 K	
1	0.152	0.638	4.923	0.524	0.697	1.773	0.913	0.737	1.017
2	0.118	0.116	1.074	0.079	0.102	1.560	0.013	0.095	8.446
3	0.115	0.082	0.933	0.069	0.078	1.642	0.017	0.065	5.305
4	0.121	0.061	1.790	0.056	0.052	3.718	0.022	0.049	8.460
5	0.332	0.085	0.939	0.174	0.057	1.351	0.022	0.047	8.365
6	0.162	0.018	1.610	0.098	0.014	2.379	0.013	0.007	8.434
		331.59 K			330.48 K			338.80 K	
1	0.221	0.671	3.870	0.635	0.698	1.467	0.960	0.819	1.079
2	0.128	0.109	0.993	0.056	0.102	2.203	0.007	0.064	9.918
3	0.124	0.080	0.904	0.051	0.078	2.223	0.009	0.060	8.667
4	0.117	0.057	1.870	0.041	0.052	5.083	0.011	0.029	9.289
5	0.242	0.066	1.079	0.142	0.057	1.656	0.009	0.025	9.098
6	0.168	0.017	1.605	0.075	0.013	2.889	0.004	0.003	10.76
		331.06 K			330.45 K				
1	0.257	0.681	3.452	0.680	0.698	1.371			
2	0.119	0.107	1.067	0.055	0.102	2.245			
3	0.119	0.079	0.946	0.050	0.078	2.270			
4	0.112	0.057	1.994	0.039	0.052	5.350			
5	0.200	0.059	1.191	0.109	0.057	2.160			
6	0.193	0.017	1.431	0.067	0.013	3.239			
		330.90 K			330.49 K				
1	0.277	0.277	0.277	0.722	0.699	1.291			
2	0.118	0.118	0.118	0.044	0.101	2.775			
3	0.116	0.116	0.116	0.043	0.078	2.636			
4	0.108	0.108	0.108	0.038	0.052	5.482			
5	0.183	0.183	0.183	0.094	0.057	2.501			
6	0.198	0.198	0.198	0.059	0.013	3.671			

Table 3. Experimental VLE Data at 101.3 kPa for the System Ethanol (1) + 3-Methylpentane (2) + *n*-Hexane (3) + *n*-Heptane (4) + Methylcyclohexane (5) + *p*-Xylene (6)

i	x_i	y_i	γ_i	x_i	y_i	γ_i	x_i	y_i	γ_i
		353.73 K			342.97 K			343.43 K	
1	0.039	0.265	6.216	0.414	0.550	1.873	0.757	0.615	1.124
2	0.130	0.208	0.957	0.087	0.131	1.231	0.033	0.106	2.589
3	0.144	0.186	0.913	0.089	0.116	1.268	0.033	0.098	2.849
4	0.150	0.088	1.025	0.091	0.054	1.496	0.037	0.048	3.219
5	0.392	0.225	1.053	0.240	0.133	1.455	0.105	0.120	2.954
6	0.145	0.028	1.226	0.079	0.016	1.971	0.035	0.013	3.547
		349.24 K			342.91 K			344.03 K	
1	0.079	0.376	5.196	0.463	0.556	1.697	0.812	0.641	1.065
2	0.124	0.178	0.976	0.082	0.130	1.298	0.025	0.099	3.136
3	0.133	0.157	0.951	0.084	0.114	1.323	0.025	0.091	3.429
4	0.143	0.073	1.036	0.084	0.053	1.594	0.028	0.045	3.904
5	0.378	0.192	1.079	0.217	0.132	1.601	0.082	0.113	3.489
6	0.143	0.024	1.244	0.070	0.015	2.091	0.028	0.011	3.661
		346.45 K			342.88 K			344.95 K	
1	0.126	0.442	4.286	0.496	0.562	1.604	0.862	0.682	1.028
2	0.128	0.165	0.950	0.076	0.125	1.348	0.016	0.084	4.045
3	0.127	0.139	0.958	0.078	0.112	1.401	0.017	0.079	4.256
4	0.132	0.066	1.116	0.077	0.052	1.708	0.020	0.042	4.939
5	0.356	0.168	1.100	0.206	0.133	1.701	0.061	0.104	4.182
6	0.131	0.020	1.290	0.067	0.016	2.333	0.024	0.009	3.366
		344.54 K			342.86 K			346.00 K	
1	0.190	0.491	3.414	0.557	0.572	1.455	0.900	0.728	1.007
2	0.125	0.148	0.923	0.066	0.122	1.516	0.013	0.069	3.965
3	0.129	0.125	0.899	0.068	0.110	1.579	0.013	0.065	4.437
4	0.124	0.061	1.174	0.068	0.051	1.899	0.015	0.038	5.744
5	0.320	0.153	1.189	0.182	0.130	1.883	0.044	0.092	4.950
6	0.112	0.022	1.793	0.059	0.015	2.486	0.015	0.008	4.588
		343.97 K			342.87 K			348.10 K	
1	0.225	0.507	3.048	0.598	0.577	1.366	0.950	0.824	0.991
2	0.116	0.141	0.964	0.060	0.121	1.653	0.006	0.041	4.800
3	0.123	0.121	0.928	0.061	0.110	1.760	0.007	0.038	4.524
4	0.117	0.058	1.207	0.062	0.051	2.082	0.007	0.025	7.533
5	0.309	0.154	1.264	0.165	0.128	2.044	0.022	0.065	6.517
6	0.110	0.019	1.614	0.054	0.013	2.353	0.008	0.007	6.920
		343.45 K			342.94 K				
1	0.279	0.525	2.601	0.651	0.586	1.271			
2	0.108	0.133	0.992	0.051	0.117	1.877			
3	0.104	0.117	1.079	0.050	0.106	2.065			
4	0.110	0.057	1.285	0.054	0.051	2.384			
5	0.295	0.149	1.304	0.146	0.126	2.269			
6	0.104	0.019	1.743	0.048	0.014	2.842			
		343.23 K			343.14 K				
1	0.318	0.534	2.342	0.711	0.601	1.183			
2	0.099	0.132	1.081	0.041	0.111	2.202			
3	0.096	0.116	1.166	0.041	0.102	2.408			
4	0.105	0.055	1.309	0.044	0.049	2.791			
5	0.282	0.145	1.338	0.123	0.124	2.632			
6	0.100	0.018	1.733	0.040	0.013	3.141			

(SUPELCO, PA/USA). The GC response peaks were integrated by using Perkin-Elmer Turbochrom software. Calibration analyses using gravimetrically prepared standard solutions were carried out to convert the peak area ratio to mole fraction of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. The uncertainty of equilibrium composition measurements was estimated to be ±0.002 mole fraction.

Results and Discussion

The isobaric $T-x-y$ data together with the activity coefficients for alcohol + hydrocarbon mixtures are presented in Tables 2−5. The alcohols investigated were

Table 4. Experimental VLE Data at 101.3 kPa for the System Propan-2-ol (1) + 3-Methylpentane (2) + *n*-Hexane (3) + *n*-Heptane (4) + Methylcyclohexane (5) + *p*-Xylene (6)

i	x_i	y_i	γ_i	x_i	y_i	γ_i	x_i	y_i	γ_i
	356.91 K			347.82 K			348.59 K		
1	0.038	0.192	4.803	0.388	0.494	1.744	0.754	0.624	1.098
2	0.146	0.237	0.889	0.090	0.151	1.188	0.032	0.101	2.356
3	0.138	0.215	1.007	0.089	0.132	1.246	0.037	0.091	2.281
4	0.148	0.076	0.809	0.088	0.054	1.307	0.037	0.048	3.116
5	0.398	0.250	1.042	0.270	0.150	1.237	0.102	0.120	2.932
6	0.132	0.030	1.279	0.075	0.019	2.026	0.038	0.016	3.282
	353.26 K			347.69 K			349.19 K		
1	0.082	0.297	3.976	0.449	0.512	1.571	0.803	0.656	1.058
2	0.136	0.218	0.972	0.080	0.141	1.253	0.026	0.090	2.356
3	0.138	0.190	0.987	0.080	0.120	1.265	0.029	0.082	2.281
4	0.146	0.070	0.850	0.081	0.057	1.505	0.030	0.046	3.116
5	0.397	0.202	0.948	0.239	0.151	1.413	0.082	0.113	2.932
6	0.101	0.023	1.472	0.071	0.019	2.151	0.030	0.013	3.282
	350.63 K			347.64 K			350.08 K		
1	0.141	0.374	3.238	0.507	0.532	1.448	0.853	0.702	1.027
2	0.132	0.202	1.000	0.700	0.131	1.281	0.026	0.092	2.348
3	0.134	0.169	0.976	0.700	0.109	1.315	0.026	0.091	2.751
4	0.132	0.060	0.880	0.074	0.056	1.622	0.031	0.050	3.181
5	0.365	0.174	0.967	0.213	0.153	1.609	0.031	0.050	3.332
6	0.096	0.021	1.566	0.066	0.019	2.319	0.033	0.015	3.324
	349.41 K			347.66 K			351.31 K		
1	0.193	0.413	2.746	0.557	0.548	1.357	0.902	0.764	1.006
2	0.131	0.176	0.909	0.062	0.127	1.457	0.013	0.054	2.661
3	0.129	0.155	0.963	0.065	0.110	1.429	0.014	0.056	3.033
4	0.125	0.062	1.001	0.066	0.054	1.752	0.016	0.034	4.021
5	0.342	0.174	1.074	0.189	0.143	1.694	0.039	0.081	4.121
6	0.080	0.020	1.877	0.061	0.018	2.375	0.016	0.011	4.792
	348.78 K			347.73 K			353.07 K		
1	0.237	0.438	2.433	0.603	0.563	1.284	0.952	0.860	0.999
2	0.117	0.158	0.930	0.055	0.122	1.575	0.007	0.030	2.612
3	0.124	0.158	1.041	0.058	0.106	1.540	0.006	0.032	3.844
4	0.113	0.059	1.076	0.060	0.053	1.887	0.008	0.022	4.908
5	0.319	0.166	1.122	0.168	0.139	1.848	0.019	0.050	4.931
6	0.090	0.021	1.796	0.056	0.017	2.436	0.008	0.006	4.884
	348.30 K			347.89 K					
1	0.289	0.461	2.142	0.654	0.580	1.212			
2	0.105	0.160	1.064	0.048	0.113	1.664			
3	0.108	0.141	1.081	0.052	0.101	1.629			
4	0.102	0.058	1.191	0.052	0.053	2.165			
5	0.305	0.161	1.157	0.145	0.136	2.083			
6	0.091	0.019	1.638	0.049	0.017	2.767			
	348.02 K			348.16 K					
1	0.337	0.478	1.972	0.703	0.601	1.155			
2	0.098	0.157	1.128	0.040	0.107	1.876			
3	0.099	0.137	1.156	0.045	0.096	1.775			
4	0.094	0.055	1.238	0.045	0.051	2.386			
5	0.290	0.154	1.175	0.123	0.129	2.309			
6	0.082	0.019	1.838	0.044	0.016	2.869			

Table 5. Experimental VLE Data at 101.3 kPa for the System 2-Methylpropan-2-ol (1) + 3-Methylpentane (2) + *n*-Hexane (3) + *n*-Heptane (4) + Methylcyclohexane (5) + *p*-Xylene (6)

i	x_i	y_i	γ_i	x_i	y_i	γ_i	x_i	y_i	γ_i
	358.80 K			350.31 K			350.85 K		
1	0.038	0.146	3.367	0.398	0.486	1.497	0.756	0.678	1.076
2	0.083	0.240	1.505	0.043	0.116	1.778	0.008	0.043	3.489
3	0.161	0.227	0.864	0.097	0.136	1.095	0.038	0.087	1.760
4	0.138	0.091	0.977	0.102	0.071	1.362	0.044	0.053	2.315
5	0.446	0.257	0.901	0.259	0.165	1.306	0.108	0.120	2.238
6	0.134	0.039	1.527	0.101	0.026	1.866	0.046	0.019	2.931
	355.20 K			350.13 K			351.31 K		
1	0.096	0.266	2.792	0.449	0.510	1.403	0.803	0.712	1.044
2	0.082	0.202	1.415	0.037	0.107	1.916	0.006	0.033	3.523
3	0.166	0.201	0.821	0.090	0.129	1.125	0.031	0.076	1.859
4	0.130	0.084	1.075	0.095	0.069	1.430	0.036	0.050	2.628
5	0.399	0.214	0.939	0.235	0.160	1.404	0.088	0.111	2.503
6	0.127	0.033	1.560	0.094	0.025	1.941	0.036	0.018	3.485
	353.52 K			350.04 K			352.10 K		
1	0.142	0.326	2.473	0.504	0.540	1.328	0.860	0.764	1.013
2	0.067	0.178	1.599	0.030	0.095	2.103	0.004	0.021	3.289
3	0.181	0.174	0.684	0.078	0.122	1.231	0.022	0.062	2.089
4	0.123	0.087	1.244	0.087	0.067	1.521	0.026	0.043	3.048
5	0.365	0.202	1.022	0.215	0.152	1.462	0.062	0.095	2.963
6	0.122	0.033	1.731	0.086	0.024	2.044	0.026	0.015	3.900
	352.32 K			350.02 K			353.06 K		
1	0.192	0.369	2.172	0.554	0.566	1.268	0.912	0.825	0.992
2	0.065	0.160	1.532	0.026	0.085	2.173	0.002	0.011	3.353
3	0.125	0.164	0.966	0.072	0.116	1.269	0.013	0.045	2.495
4	0.122	0.085	1.275	0.078	0.063	1.596	0.017	0.034	3.571
5	0.367	0.188	0.984	0.193	0.147	1.576	0.039	0.073	3.509
6	0.129	0.034	1.767	0.077	0.023	2.190	0.017	0.012	4.598
	351.40 K			350.09 K			354.04 K		
1	0.252	0.410	1.908	0.606	0.593	1.211	0.954	0.891	0.985
2	0.063	0.140	1.420	0.021	0.076	2.401	0.002	0.008	2.669
3	0.117	0.151	0.976	0.063	0.111	1.384	0.008	0.026	2.278
4	0.121	0.080	1.247	0.069	0.061	1.743	0.009	0.022	4.226
5	0.324	0.189	1.154	0.173	0.140	1.671	0.020	0.047	4.269
6	0.123	0.030	1.694	0.068	0.019	2.043	0.007	0.006	5.378
	350.96 K			350.24 K					
1	0.294	0.434	1.763	0.658	0.621	1.160			
2	0.055	0.129	1.518	0.015	0.064	2.818			
3	0.111	0.146	1.008	0.053	0.102	1.506			
4	0.116	0.077	1.271	0.061	0.058	1.865			
5	0.304	0.183	1.208	0.152	0.134	1.812			
6	0.120	0.031	1.825	0.061	0.021	2.502			
	350.58 K			350.49 K					
1	0.345	0.460	1.617	0.708	0.650	1.117			
2	0.048	0.123	1.676	0.011	0.055	3.279			
3	0.103	0.141	1.060	0.045	0.094	1.622			
4	0.104	0.076	1.417	0.053	0.055	2.018			
5	0.295	0.174	1.199	0.129	0.126	1.991			
6	0.105	0.026	1.776	0.054	0.020	2.665			

mostly used as additives in gasoline, i.e., methanol and ethanol, or have been more extensively tested as possible fuel additive candidates, e.g., propan-2-ol and 2-methylpropan-2-ol. The hydrocarbon mixture consists of *n*-hexane, *n*-heptane, 3-methylpentane, methylcyclohexane, and *p*-xylene. The vapor-phase coefficients were calculated from the Soave−Redlich−Kwong (SRK) equation of state,[4] where the binary interaction parameter, k_{ij}, was set to be 0. The fugacity coefficients estimated by this method lie between 1.00 and 0.97. The Poynting correction can be also taken as unity for the experimental conditions in this study. Thus, the activity coefficients γ_i of the pure component were calculated by the equation

$$\gamma_i = Py_{i}/P_i^0 x_i \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions of the component in equilibrium and P is the system total pressure. The vapor pressures of the pure components, P_i^0, were obtained from the equation constants compiled by Reid et al..[5] The calculated activity coefficients are estimated to be accurate to within 3%.

Table 6 gives the equilibrium boiling temperatures, equilibrium compositions of alcohol, and the relative volatilities of alcohol (α_1) with respect to the hydrocarbon mixture. The relative volatility of alcohol is defined by the equation

$$\alpha_1 = \frac{y_1/(1 - y_1)}{x_1/(1 - x_1)} \tag{2}$$

where x_1 and y_1 are the equilibrium liquid-phase and vapor-phase mole fractions of alcohol, respectively. Figure 1 graphically represents the experimental $T-x_1-y_1$ data for each of the systems. It can be observed that all the systems show a minimum boiling temperature. This kind of behavior seems to be characteristic for alcohol + hydrocarbon mixtures.[6−9] The relative volatilities of alcohol were plotted

Table 6. Equilibrium Boiling Temperatures, Vapor−Liquid Compositions of Alcohols, and Relative Volatilities of Alcohol for Alcohol (1) + Hydrocarbon Mixtures at 101.3 KPa

T (K)	x_1	y_1	α_1	T (K)	x_1	y_1	α_1
	methanol				ethanol		
363.04[a]	0.000	0.000		363.04[a]	0.000	0.000	
352.96	0.018	0.268	19.68	353.73	0.039	0.265	8.80
346.42	0.042	0.420	16.41	349.24	0.079	0.376	7.00
340.30	0.074	0.536	14.36	346.45	0.126	0.442	5.52
333.63	0.153	0.638	9.83	344.54	0.190	0.491	4.12
331.59	0.222	0.671	7.22	343.97	0.225	0.507	3.54
331.06	0.257	0.681	6.18	343.45	0.279	0.525	2.85
330.90	0.271	0.684	5.82	343.23	0.318	0.534	2.46
330.58	0.359	0.694	4.05	342.97	0.414	0.550	1.73
330.56	0.366	0.694	3.94	342.91	0.463	0.556	1.45
330.54	0.503	0.697	2.27	342.88	0.496	0.562	1.30
330.50	0.524	0.697	2.09	342.86	0.557	0.572	1.06
330.48	0.635	0.697	1.32	342.87	0.598	0.577	0.92
330.45	0.680	0.698	1.09	342.94	0.651	0.586	0.76
330.49	0.722	0.699	0.89	343.14	0.711	0.601	0.61
330.59	0.758	0.699	0.74	343.43	0.757	0.615	0.51
330.69	0.808	0.701	0.56	344.03	0.812	0.641	0.41
331.03	0.863	0.703	0.38	344.95	0.862	0.682	0.34
331.87	0.913	0.737	0.27	346.00	0.900	0.728	0.30
333.84	0.960	0.819	0.18	348.10	0.950	0.824	0.25
337.56	1.000	1.000		351.43	1.000	1.000	
	propan-2-ol				2-methylpropan-2-ol		
363.04[a]	0.000	0.000		363.04[a]	0.000	0.000	
356.91	0.038	0.192	5.97	358.80	0.038	0.146	4.30
353.26	0.082	0.297	4.75	355.20	0.096	0.266	3.41
350.63	0.141	0.374	3.62	353.52	0.142	0.323	2.90
349.41	0.193	0.413	2.94	352.32	0.192	0.369	2.46
348.78	0.237	0.438	2.51	351.40	0.252	0.410	2.06
348.30	0.289	0.461	2.10	350.96	0.294	0.434	1.84
348.02	0.337	0.478	1.80	350.58	0.345	0.460	1.62
347.82	0.388	0.494	1.54	350.31	0.398	0.486	1.43
347.69	0.449	0.512	1.29	350.13	0.449	0.510	1.27
347.64	0.507	0.532	1.11	350.04	0.504	0.540	1.16
347.66	0.557	0.548	0.96	350.02	0.554	0.566	1.05
347.73	0.603	0.563	0.84	350.09	0.606	0.593	0.95
347.89	0.654	0.580	0.73	350.24	0.658	0.621	0.85
348.16	0.703	0.601	0.63	350.49	0.708	0.650	0.77
348.59	0.754	0.624	0.54	350.85	0.756	0.678	0.68
349.19	0.803	0.656	0.47	351.31	0.803	0.712	0.61
350.08	0.853	0.702	0.41	352.10	0.860	0.764	0.52
351.31	0.902	0.765	0.35	353.06	0.912	0.826	0.45
353.07	0.952	0.860	0.31	354.04	0.954	0.891	0.40
355.39	1.000	1.000		355.47	1.000	1.000	

[a] Equilibrium boiling temperature of the base fuel at 101.3 kPa.

as a function of alcohol mole fraction in Figure 2. The values of α_1 at $x_1 < 0.5$ follow the order: methanol > ethanol > propan-2-ol > 2-methylpropan-2-ol. However, the values of α_1 at $x_1 > 0.6$ are varied according to the following order: 2-methylpropan-2-ol > propan-2-ol > ethanol. The system containing methanol has the highest values in α_1 at $x_1 < 0.8$ and has the smallest values in α_1 after $x_1 \approx 0.9$.

The compositions where the minimum boiling temperatures occurred have been obtained, in all cases, by determining the x_1 values that make the function $(x_1 - y_1) = f(x_1)$ equal zero. The minimum boiling temperatures were then computed from a cubic polynomial equation, $T = f(x_1)$, whose coefficients were obtained by fitting the experimental results around the minimum boiling temperature, using the x_1 values previously determined. The minimum boiling temperatures and the corresponding compositions for the alcohol + hydrocarbon mixtures are $T = 330.47$ K and $x_1 = 0.699$ for methanol, $T = 342.86$ K and $x_1 = 0.574$ for ethanol, $T = 347.65$ K and $x_1 = 0.544$ for propan-2-ol, and $T = 350.04$ K and $x_1 = 0.579$ for 2-methylpropan-2-ol.

The boiling temperature of the system was correlated with its liquid-phase concentration of alcohol in mole fraction by the equation proposed by Wisniak and Tamir,[10]

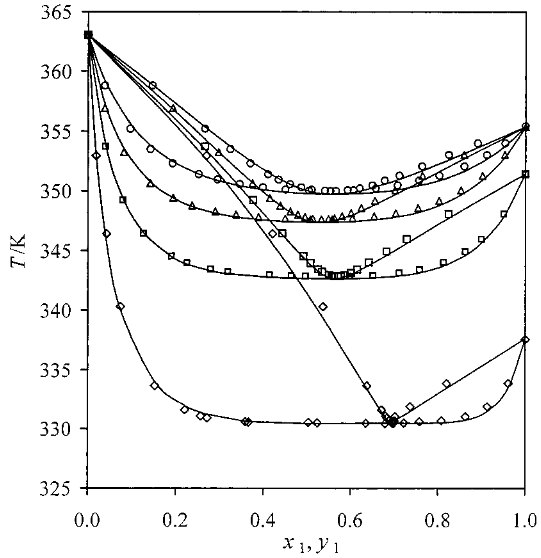

Figure 1. Experimental $T-x_1-y_1$ diagram for alcohol + hydrocarbon mixtures at 101.3 kPa: (◇) methanol; (□) ethanol; (△) propan-2-ol; (○) 2-methylpropan-2-ol.

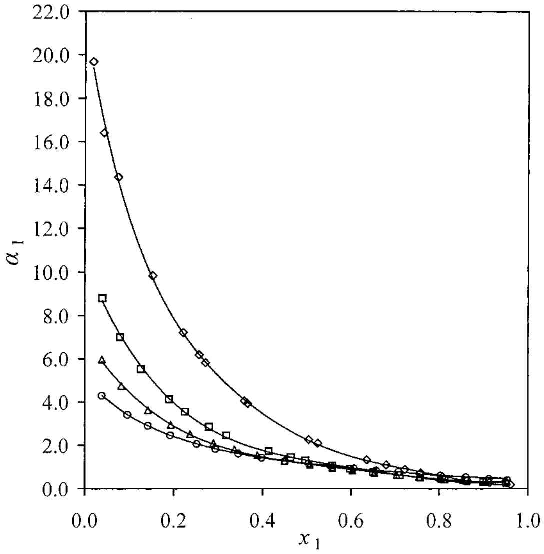

Figure 2. Relative volatilities of alcohol as a function of liquid-phase mole fraction of alcohol for alcohol + hydrocarbon mixtures at 101.3 kPa: (◇) methanol; (□) ethanol; (△) propan-2-ol; (○) 2-methylpropan-2-ol.

$$T = x_1T_1 + (1 - x_1)T_2 + x_1(1 - x_1)\sum_{k=0}^{3} a_k(2x_1 - 1)^k \quad (3)$$

where T_1 is the boiling temperature of alcohol, T_2 is the equilibrium boiling temperature of the base fuel, and a_k are the coefficients. The vapor-phase mole fraction of the mixture was also fitted with its liquid-phase mole fraction by a Redlich−Kister-type equation,[11]

$$y_1 - x_1 = x_1(1 - x_1)\sum_{k=0}^{3} a_k(2x_1 - 1)^k \quad (4)$$

The values of coefficients a_k of eqs 3 and 4 were determined by a multiple regression analysis based on the least-squares method and are summarized along with the

Table 7. Results in Correlation of Boiling Temperatures and Vapor-Phase Compositions of Alcohol for Alcohol + Hydrocarbon Mixtures

system	a_0	a_1	a_2	a_3	σ
Wisniak−Tamir, eq 3 for Boiling Temperature					
methanol	−73.16	38.00	−147.75	110.50	1.57
ethanol	−55.27	14.87	−84.48	59.76	0.70
propan-2-ol	−45.02	10.69	−53.87	39.09	0.39
2-methylpropan-2-ol	−36.19	11.31	−33.08	23.56	0.20
Redlich−Kister, eq 4 for Vapor-Phase Composition of Alcohol					
methanol	70.46	125.65	156.53	557.31	0.040
ethanol	21.08	141.36	75.45	308.24	0.018
propan-2-ol	8.98	121.90	50.95	206.99	0.011
2-methylpropan-2-ol	13.76	89.65	41.92	145.10	0.006

standard deviations between the experimental and fitted values of the respective functions in Table 7. The standard deviation (σ) is defined by

$$\sigma = [\sum_{i=1}^{m}(Y_{\mathrm{i}}^{\mathrm{exp}} - Y_{\mathrm{i}}^{\mathrm{calc}})^2/(m - 4)]^{1/2} \qquad (5)$$

where m is the number of experimental points. The largest standard deviations occurred for the methanol system with 1.57 K for boiling temperature and 0.040 for vapor-phase composition.

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